Electronic Supplementary Information

Precise synthesis of rod-coil type miktoarm star copolymer containing poly(*n*-hexyl isocyanate) and aliphatic polyester

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Table S1. Synthesis of PHIC macroinitiators (PHIC-OH, PHIC-$(OH)_2$, and PHIC-$(OH)_3$) via CuAAC reaction of PHIC-N_3 with ethynyl alcohol derivatives.[a]

PHIC-N_3		PHIC macroinitiators		
$M_{n,NMR}$[b]	M_w/M_n[c]	Structure	$M_{n,NMR}$[b]	M_w/M_n[c]
3,000	1.07	PHIC-OH	3,100	1.07
5,000	1.06		5,100	1.06
10,300	1.13		10,300	1.13
11,400	1.18		11,400	1.19
3,000	1.07	PHIC-$(OH)_2$	3,100	1.07
5,000	1.06		5,100	1.06
10,900	1.10		10,900	1.13
11,300	1.18		11,300	1.19
3,000	1.07	PHIC-$(OH)_3$	3,200	1.07
5,000	1.07		5,200	1.06
9,600	1.16		9,600	1.16
11,300	1.19		11,300	1.18

[a] Synthesis conditions: solvent, dry THF; catalyst, CuCl, PMDETA; [ethynyl derivatives]/[PHIC-N_3]/[CuCl]/[PMDETA] = 3.5/1.0/3.0/6.0 ; reaction time, 48 h; temp., r.t. [b] Determined by ^{1}H NMR spectrum in $CDCl_3$. [c] Determined by SEC in THF using PSt standards.

Table S2. Solubility of PHIC-*b*-PLLA$_{1\sim3}$, PHIC-*b*-PCL$_{1\sim3}$, and homopolymers [a]

Polymer	$M_{n,NMR}$ [b] (M_w/M_n [c])	f_{PHIC} [d]	$CHCl_3$	THF	DMF	Hexane
PLLA	10,200 (1.08)	–	○	○	○	×
PCL	10,500 (1.04)	–	○	○	○	×
PHIC	10,400 (1.11)	1.00	○	○	×	○
PHIC-*b*-PLLA	19,200 (1.07)	0.59	○	○	○	×
PHIC-*b*-PLLA$_2$	20,700 (1.12)	0.59	○	○	○	×
PHIC-*b*-PLLA$_3$	19,700 (1.08)	0.54	○	○	○	×
PHIC-*b*-PCL	20,900 (1.07)	0.53	○	○	○	×
PHIC-*b*-PCL$_2$	22,200 (1.17)	0.53	○	○	○	×
PHIC-*b*-PCL$_3$	20,600 (1.09)	0.50	○	○	○	×

[a] Conditions: temp., r.t.; concentration, 0.1 ($g \cdot L^{-1}$); ○, soluble; ×, insoluble. [b] Determined by ^1H NMR spectrum in $CDCl_3$. [c] Determined by SEC in THF using PSt standards. [d] $f_{PHIC} = (M_{n,NMR,PHIC} \times d_{PLLA\ or\ PCL})/(M_{n,NMR,PHIC} \times d_{PLLA\ or\ PCL} + M_{n,NMR,PLLA\ or\ PCL} \times d_{PHIC})$, $d_{PHIC} = 1.0$, $d_{PLLA} = 1.20$, and $d_{PCL} = 1.15$.

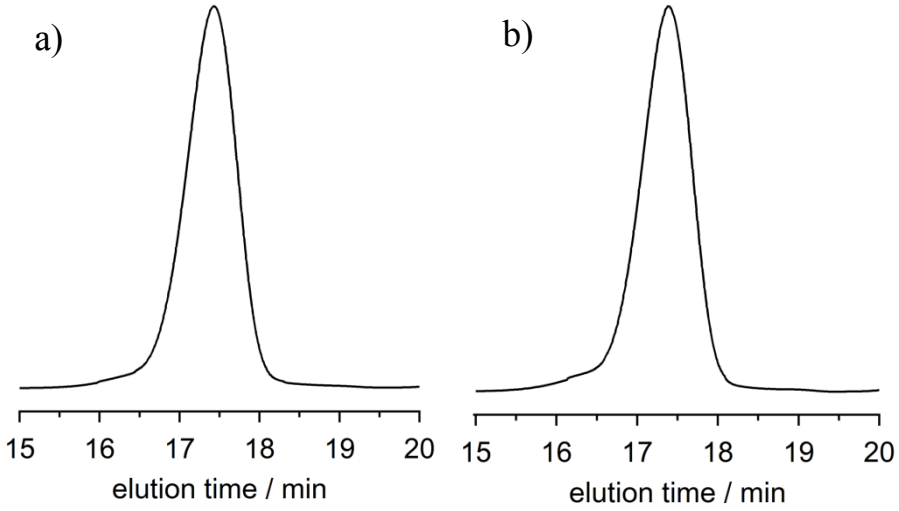

Figure S1. SEC traces of PHIC-$(OH)_2$ (a, $M_{n,NMR}$ = 5,100, $M_{w,SEC}$ = 6,100, M_w/M_n = 1.06) and PHIC-$(OH)_3$ (b, $M_{n,NMR}$ = 5,200, $M_{w,SEC}$ = 5,900, M_w/M_n = 1.06) (flow rate, 1.0 mL·min^{-1}; solvent: THF).

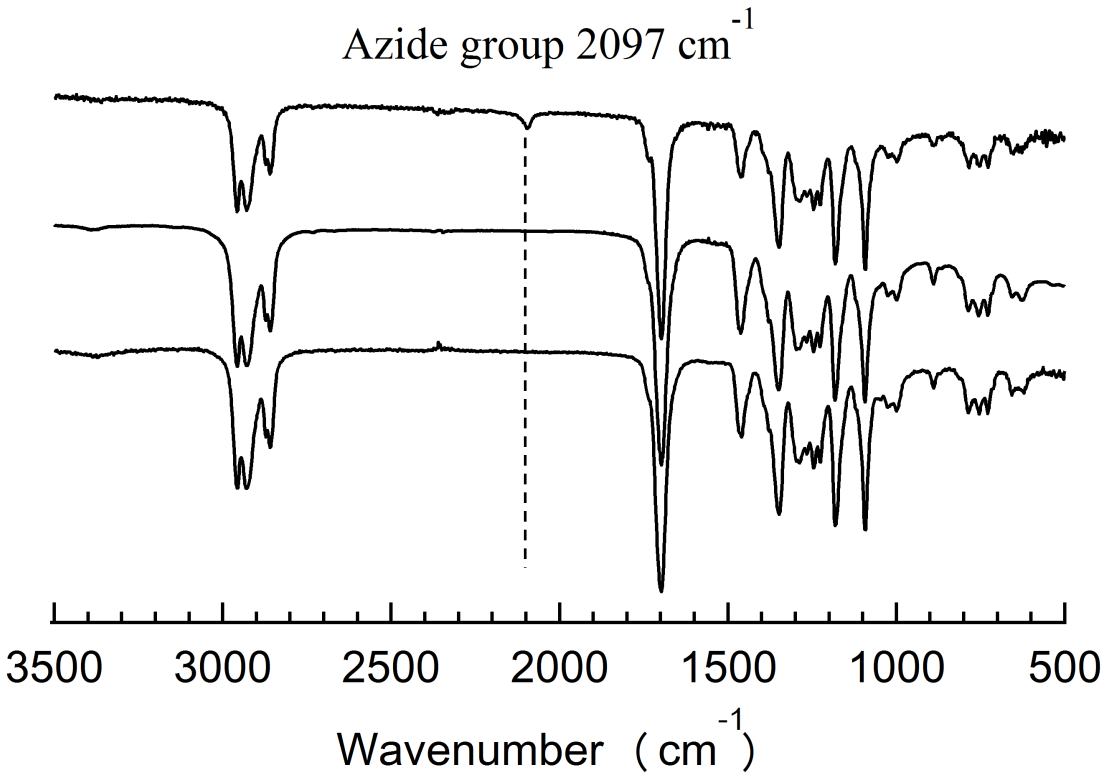

Figure S2. FT-IR spectra of PHIC-N_3 (upper), PHIC-$(OH)_2$ (middle) and PHIC-$(OH)_3$(lower).

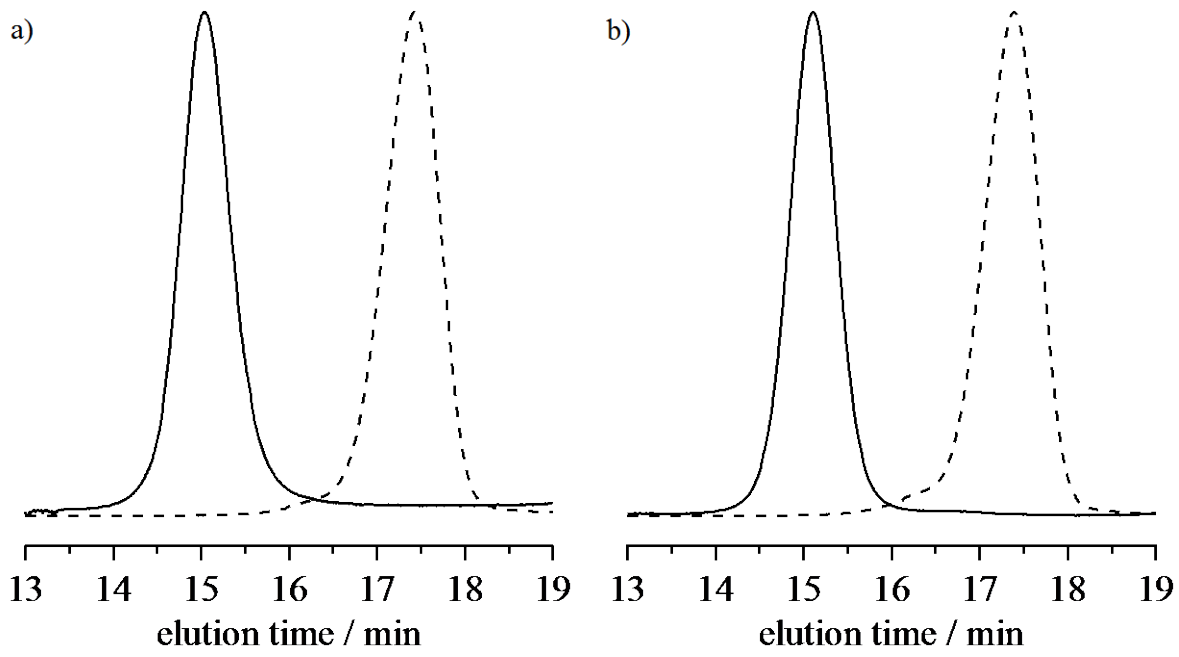

Figure S3. SEC traces detected by RI detector (eluent, THF; flow rate, 1.0 mL·min^{-1}). a) PHIC-*b*-PLLA$_2$ (solid line, $M_{n,NMR}$ = 20,000, $M_{w,SEC}$ = 23,300, M_w/M_n = 1.09) and PHIC-(OH)$_2$ (dashed line, $M_{n,NMR}$ = 5,100, M_w/M_n = 1.06), b) PHIC-*b*-PLLA$_3$ (solid line, $M_{n,NMR}$ = 20,200, $M_{w,SEC}$ = 22,800, M_w/M_n = 1.08) and PHIC-(OH)$_3$ (dashed line, $M_{n,NMR}$ = 5,200, M_w/M_n = 1.06).

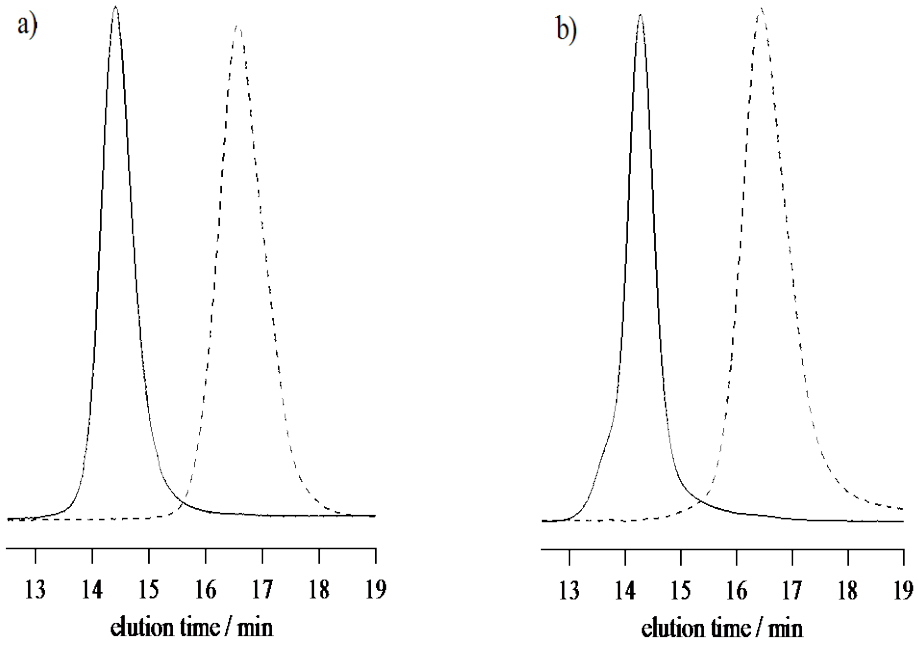

Figure S4. SEC traces detected by RI detector (eluent, THF; flow rate, 1.0 mL·min^{-1}). a) PHIC-*b*-PCL$_2$ (solid line, $M_{n,NMR}$ = 21,700, $M_{n,SEC}$ = 35,700, M_w/M_n = 1.06) and PHIC-(OH)$_2$ (dashed line, $M_{n,NMR}$ = 5,500, M_w/M_n = 1.10), b) PHIC-*b*-PCL$_3$ (solid line, $M_{n,NMR}$ = 23,600, $M_{n,SEC}$ = 37,600, M_w/M_n = 1.09) and PHIC-(OH)$_3$ (dashed line, $M_{n,NMR}$ = 5,600, M_w/M_n = 1.11).

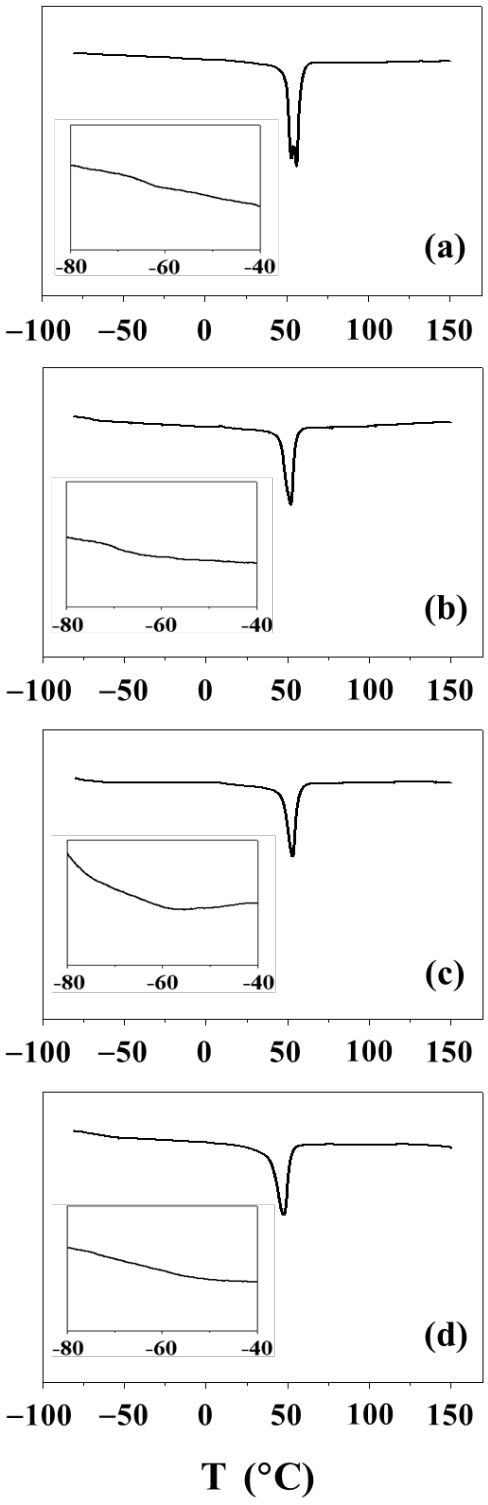

Figure S5. DSC results of PCL and PHIC-*b*-PCL$_{1\sim3}$, which were measured during heating run with a rate of 10.0 °C min^{-1} after quenched to −100 °C from the melt: (a) PCL (M_n = 10,000); (b) PHIC-*b*-PCL ($M_{n,NMR}$ = 22,200, M_w/M_n = 1.17, f_{PHIC} = 0.55); (c) PHIC-*b*-PCL$_2$ ($M_{n,NMR}$ = 23,000, M_w/M_n = 1.12, f_{PHIC} = 0.53); (d) PHIC-*b*-PCL$_3$ ($M_{n,NMR}$ = 22,200, M_w/M_n = 1.14, f_{PHIC} = 0.54).

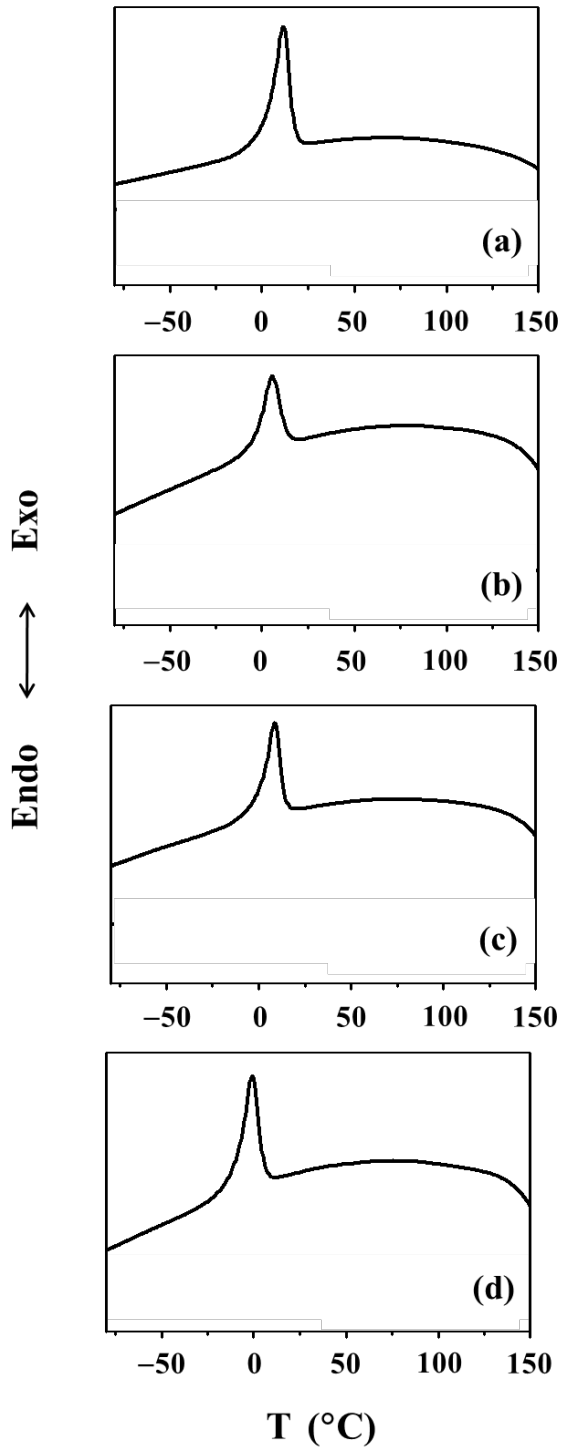

Figure S6. DSC results of PCL and PHIC-*b*-PCL$_{1\sim3}$, which were measured during quenching from from the melts: (a) PCL (M_n = 10,000); (b) PHIC-*b*-PCL ($M_{n,NMR}$ = 22,200, M_w/M_n = 1.17, f_{PHIC} = 0.55); (c) PHIC-*b*-PCL$_2$ ($M_{n,NMR}$ = 23,000, M_w/M_n = 1.12, f_{PHIC} = 0.53); (d) PHIC-*b*-PCL$_3$ ($M_{n,NMR}$ = 22,200, M_w/M_n = 1.14, f_{PHIC} = 0.54).